

Use Of Zinc Oxide as Catalyst to Remove Textile Effluents With Photo Catalysis Based Treatment Plant

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Abstract: The most crucial resource for each living organism on this planet is clean and drinking water. Textile goods are another crucial resource for human life. Most human activities, including the textile industry, create wastes that can have a significant impact on water quality in today's world. The textile industry's effluents are mostly organic and contain color. Many traditional methods for treating this wastewater are currently in use, and researchers are developing new and improved approaches to improve the quality of treatment. photo catalysis-based treatment system was created in order to treat textile wastewater in this study. The catalyst employed in this plant was Zinc Oxide (ZnO).. Because the beneficial effects of photocatalysis on textile effluents have been explored in many ways, a rotating reactor was created for this investigation. The percentage change in COD, pH, TSS, and TDS concentrations was used to evaluate the treatment's quality. For galvanised iron plates, the percentage reduction in pH, BOD, TDS, and TSS is best for a 4-hour retention time, and any longer retention time did not result in any meaningful changes.

Keywords: Nanotechnology , zinc oxide , Wastewater treatment , Pollutants , Photo Catalysis Based Treatment Plant , Textile Effluents

1 INTRODUCTION

One of the biggest concerns in today's world is water. Due to the increasing population, people living in remote places are unable to fulfill their crucial requirement of clean drinking water and even in big cities, most population do not get even proper drinking water or get contaminated drinking water. Irrespective of the fact that water covers almost 71% of Earth's surface, most of the water available is either too saline or too polluted to be used in human consumption this type of contaminated, non-drinkable water is known as wastewater. Waste water is any water that has been affected by human use. Wastewater is "used water from any combination of domestic, industrial, commercial or agricultural activities, surface runoff and any sewer inflow or sewer infiltration. K. Byrappa, et al (2006) , M.A. Behnajady et al (2006) and N. Daneshvar et al (2004) reported that textile industry has for a long period of time been one of the largest of water user and polluters and in comparison to their rate and quantity of developing waste effluent, the treatment units and methods are not equally developed. [1,2,3]

Dehghani, M. H., & Mahdavi, P. (2015) determined that the photocatalytic process of zinc oxide nanoparticles in the UV reactor effectively removed the acid red 4092 dye from an aqueous solution. Tarun Gehlot et al (2021) predicted value of BOD and COD by model and regression analysis was in close agreement with their respective measured value. It was found that the pH parameter has more effect on BOD and COD as compared to predicting another parameter. [4,5]

Al-Buriahi, A. K. et al (2022). revealed a strong correlation between the concentration of ZnO NPs and the photocatalysis efficiency ($R = 0.72$). These findings reveal that man-sized photocatalysts have a high potential for removing RhB from the wastewater. Abdullah, F. H., Bakar, N. A., & Bakar, M. A. (2022). reviewed and summarized the recent advances in the fabrication, modification, and industrial application of ZnO photocatalyst based on the analysis of the latest studies. [6,7]

Jodhpur has number of textile industries generating huge amount of waste water. Efficient treatment of this waste is a problem since last many years. Main issue in treatment is reduction in COD, as this is because of presence of complex dyes in waste water. Hence, COD reduction using ZnO as a nano reactorial has been taken as main parameter in this study.

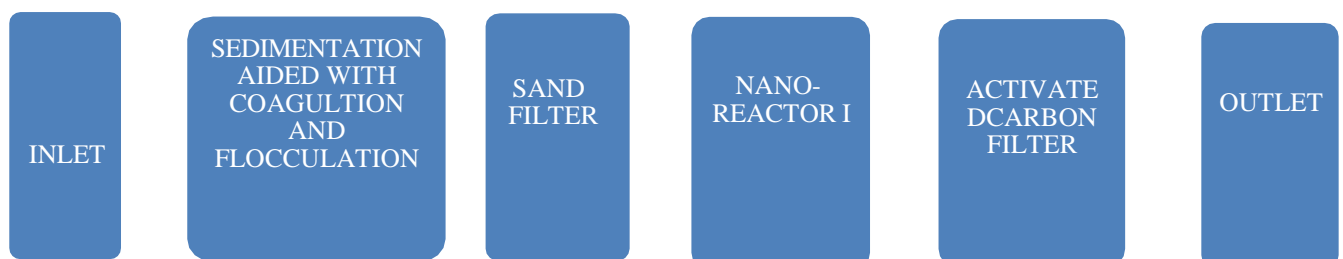


Figure 1 : Process flow chart

2 MATERIALS & METHODS

Samples for BOD analysis may degrade significantly during storage between collection and analysis, resulting in low BOD values. Minimize reduction of BOD by analyzing sample promptly or by cooling it to near-freezing temperature during storage. However, even at low temperature, keep holding time to a minimum. Warm chilled samples to $20 \pm 3^\circ\text{C}$ before analysis.

Apparatus

- Incubation bottles:* Use glass bottles having 60 mL or greater capacity (300-mL bottles having a ground-glass stopper and a flared mouth are preferred). Clean bottles with a detergent, rinse thoroughly, and drain before use.
- Air incubator or water bath, thermostatically controlled at $20 \pm 1^\circ\text{C}$. Exclude all light to prevent possibility of photosynthetic production of DO.

Reagents

- Phosphate buffer solution: Dissolve 8.5 g KH_2PO_4 , 21.75 g K_2HPO_4 , 33.4 g $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$, and 1.7 g NH_4Cl in about 500 mL distilled water and dilute to 1 L. The pH should be 7.2 without further adjustment. Alternatively, dissolve 42.5 g KH_2PO_4 or 54.3 g K_2HPO_4 in about 700 mL distilled water. Adjust pH to 7.2 with 30% NaOH and dilute to 1 L.
- Magnesium sulfate solution: Dissolve 22.5 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in distilled water and dilute to 1 L.
- Calcium chloride solution: Dissolve 27.5 g CaCl_2 in distilled water and dilute to 1 L.
- Ferric chloride solution: Dissolve 0.25 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in distilled water and dilute to 1 L.
- Alkali-iodide-azide reagent: Dissolve 500 gm of sodium hydroxide (NaOH), and 135 gm of sodium iodide (NaI) in distilled water. Make up the solution to 1000 mL of distilled water. Now dissolve 10 gm of sodium azide in this solution.
- Starch: Use either an aqueous solution or soluble starch powder mixtures. To prepare an aqueous solution, dissolve 2 g laboratory-grade soluble starch and 0.2 g salicylic acid, as a preservative, in 100 mL hot distilled water.
- Standard sodium thiosulfate titrant: Dissolve 6.205 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in distilled water. Add 1.5 mL 6N NaOH or 0.4 g solid NaOH and dilute to 1000 mL. Standardize with bi-iodate solution.
- Dilution water: Add 1 ml of each potassium phosphate, magnesium sulfate, calcium chloride and ferric chloride solution per 1 L of dilution water and saturate the water with oxygen for a minimum time of 2 hours.

Procedure

- Take 300 mL sample in BOD bottle. Prepare two sets of this sample. Keep one set for DO analysis for day 0 (i.e., Sample 0 Day) and another sample in BOD incubator for 5 days at 20°C
- For a given sample bottle, add 1 mL of alkali azide and then 1 mL manganous sulfate solution. Shake well the bottle and keep it open for 5 minutes to settle the precipitate. Add 2 mL concentrated H_2SO_4 and place the cap on the bottle. Shake well the bottle till all the precipitate is dissolved.
- Take 203 mL of sample in conical flask and titrate with standard sodium thiosulfate solution (0.025N) till the colour changes from dark yellow to light yellow. Then add few drops of starch indicator and continue to titrate till the color of the solution becomes either colorless. Note down volume of 0.025N sodium thiosulfate consumed.
- Calculate the DO of the sample.

Dissolved oxygen (DO) (in mg/L) = mL of sodium thiosulfate (0.025N) consumed.

Calculation

$$\text{BOD}_5, \text{ mg/L} = \frac{D_1 - D_2}{P}$$

Where D_1 = DO of diluted sample immediately after preparation, mg/L, D_2 = DO of diluted sample after 5 d incubation at 20°C , mg/L, P = decimal volumetric fraction of sample used

3 EXPERIMENTAL PROGRAMME & RESULTS

A pilot scale treatment plant was setup in the premises of the Common Effluent Treatment Plant (CETP), Jodhpur Pradyushan Nivaran Trust (JPNT), Jodhpur for the treatment of textile waste water.

This plant consists of overall 4 units which in a sequence are: -

- Coagulation and flocculation chamber

- Sand filter
 - ZnO Nano Reactor 1
 - Activated carbon unit
- Steps involved:
- Raw wastewater from equalization tank of CETP was taken for treatment.
 - Wastewater was allowed to pass through various units of the pilot plant, for different HLR in the ZnO nanoreactor.
 - Effluent from each unit was collected for the analysis of parameters i.e. pH, TDS, TSS, and BOD.
 - Results were analyzed.

Coagulation and flocculation chamber :The process of treatment in the plant starts with a coagulation and flocculation chamber. For this purpose, sedimentation tank was built with the holding capacity of 150 liters. Optimum coagulant dose was determined by jar test. Hand held stirrer was used to maintain a constant rotation.

- Wastewater was collected from the equalization tank present in the premises of JPNT, Jodhpur.
- A sample (named 01) was collected from this point for analysis.
- The coagulant is then mixed and the water is allowed to settle for 30 minutes.
- The second sample (named 02) was collected after settling the supernatant liquid.
- The supernatant liquid was allowed to pass through the sand filter.

Sand filter :The filter was designed as follow: -Assuming

HLR = $3.5 \text{ m}^3/\text{m}^2/\text{day}$ diameter of filter = 0.4 m.

Then $Q = .0011 \text{ m}^3/\text{minute}$.

The unit in the series is the gravity sand filter. It made of sand, coarse and fine aggregate.

The depth of each layer was kept as follows: -

- Sand: - 7.6 cm
- Coarse aggregate: - 11.4 cm

Fine aggregate: - 11.4 cm The outlet of this unit was named sample 03 passed further to the Nano reactor.

Nano Material unit

The main ingredient of the plant is the treatment unit based on photocatalysis of water on a ZnO semiconductor fabricated flat plate. It's a rotating flat plate type reactor.

- The plates used in it are first coated with ZnO Nanoreactor and then is attached to an axle rotating at the speed of 2-3 rpm.
- The effluent of the sand filter is then poured in it and is kept for a retention time of 2 hours, 4 hours, 6 hours and 8 hours. Out of these 4 hours proved to be the most fruitful period and hence was finally selected.
- Galvanized iron sheets were used as a substrate or base for the ZnO fabrication. And the ZnO nanocrystals were fabricated by a sol-gel method in the following manner: -
- First of all, a coating solution is prepared by adding 400ml of Isopropyl alcohol, 250ml Methanol and 1.43 gm Zinc acetate (.019 M) this is then allowed to stir for 30 minutes.
- Simultaneously, a saline solution is prepared by adding 350ml De-ionised water with .4 gm Sodium hydroxide and stirring it for almost 30 minutes.
- The coating solution is then kept on a hot plate at 65°C , constantly stirred and the saline solution is added dropwise such that the whole solution takes 3 hours to get mixed.
- This solution is then mixed thoroughly in a sonicator (at 45°C , 17s-3s pulse, for 20 minutes),
- The Galvanized iron sheet is then placed on a hot plate at 200°C and the prepared solution is then coated on it.
- Simultaneous a Nano growth solution is prepared in which 3 gm Zinc Nitrate (.015 M solution) and 7 gm Hexamine (.05 M solution) is added in 1 liter of water and is stirred for 20 minutes.
- The coated plates placed in a container.
- The container is then filled with the growth solution to such a level that the plate gets completely submerged into it.

- This container is then kept inside an oven and heated at a temperature of 90 and is allowed to stand that way for almost 2 hours.
- The plates are then taken out and dried.

These plates are then attached to two rotating units hence making them into the 2 nanounits which are as follows

Nano Reactor 01

outlet of the sand filter is received by this unit. It further uses photocatalysis to treat the sample. Its outlet is then fed to the activated carbon filter.

Activated Carbon Unit

The filter was designed as follows:-HLR= 9.38m³/m²/day

Diameter of filter =0.4 m Then Q = 1.6 m³/day

EBCT calculated = 40.5 minutes

Activated carbon filter was made of carbon ,fine aggregate, coarse aggregate.

The depth of each layer was kept as follows :

- Carbon:- 15 cm
- Fine aggregate:- 7.6 cm
- Coarse aggregate: - 7.6 cm

.This outlet was the final treated water and was named as sample 06.

The treatment plant was operated for different intervals of 2 hours, & 4 hours with different coagulants ,all testing of COD was done at JPNT, Jodhpur.

Observation Set 1: -

Table 1: observation data for set 1

Parameter	Raw	After coagulation & flocculation	After sand filter	After nanoreactor (Detention time = 2 hr)	After activated carbon filter
BOD (mg/l)	760	530	440	105	85
pH	9.1	8.9	8.3	8.5	8.6
TSS (mg/l)	1363	260	60	58	10
TDS (mg/l)	3710	3270	2910	2910	2880

Table 2: percentage reduction after individual treatment for set 1, HRT = 2 hr

Parameter	% change from raw to C & F	% change from C & F to sand filter	% change from sand filter to nanoreactor	% change from nanoreactor to ACF	Overall reduction
BOD (mg/l)	30.26	16.98	76.13	19.04	88.81
pH	2.19	6.74	-2.40	-1.18	5.49
TSS (mg/l)	80.92	76.92	3.33	82.75	99.26
TDS (mg/l)	11.85	11	0	1.03	22.37

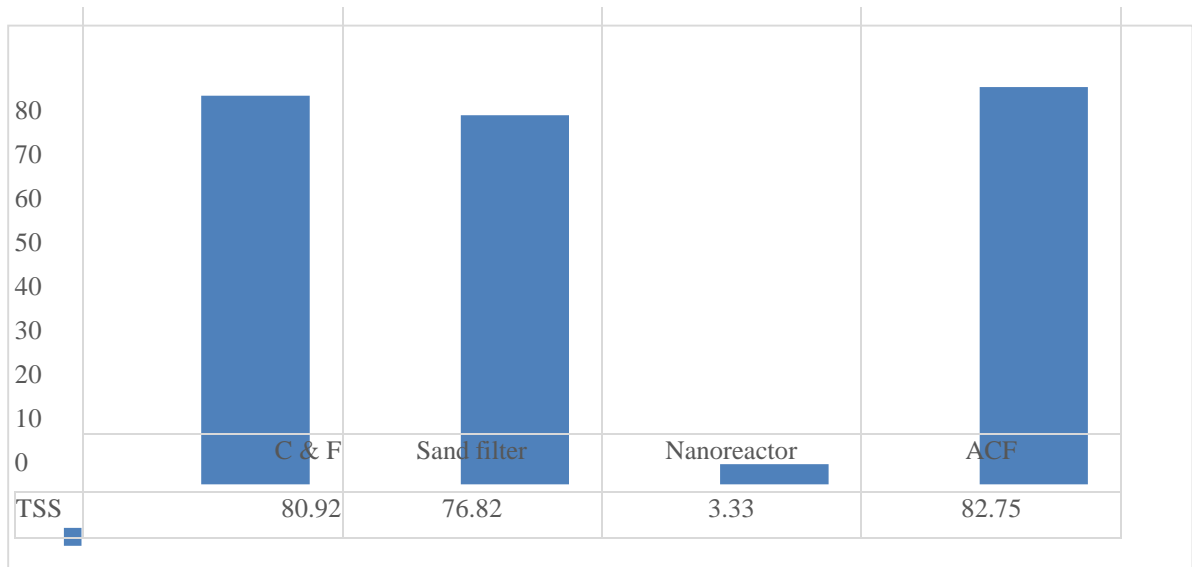


Figure 4: percentage change in TSS for observation set 1

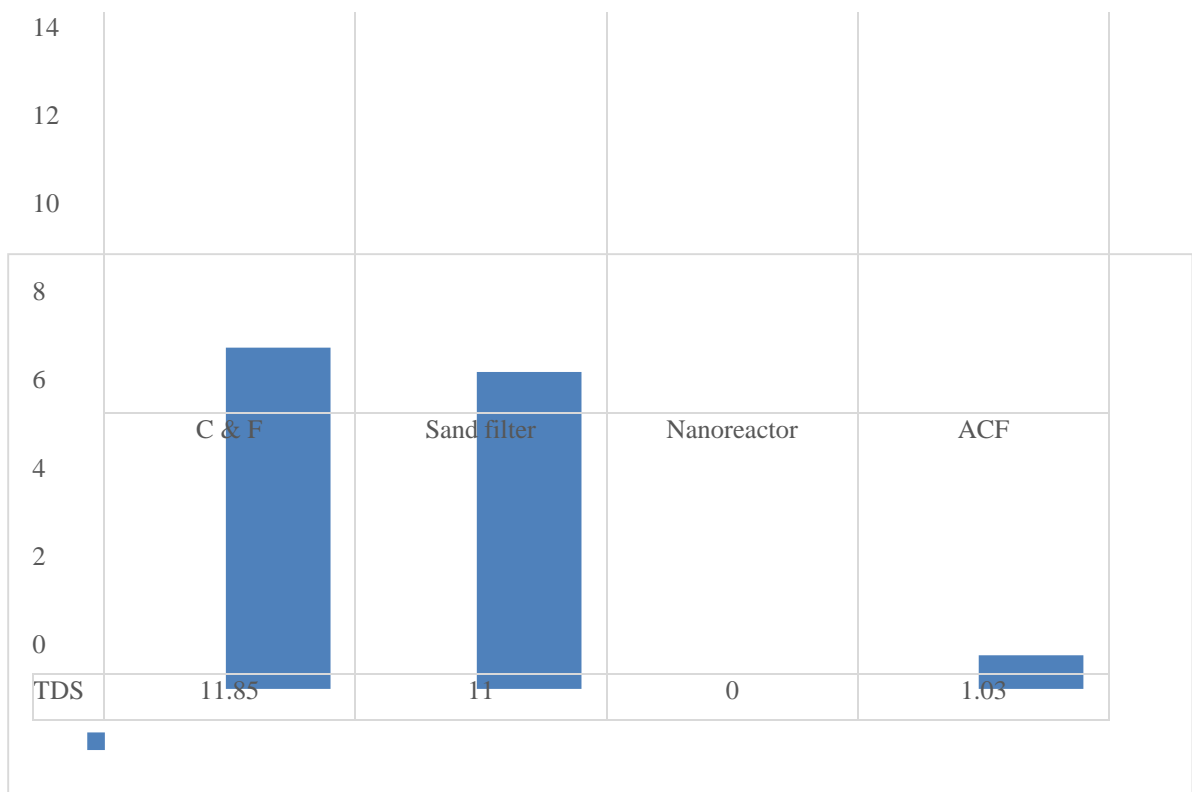


Figure 5: percentage change in TDS for observation set 1

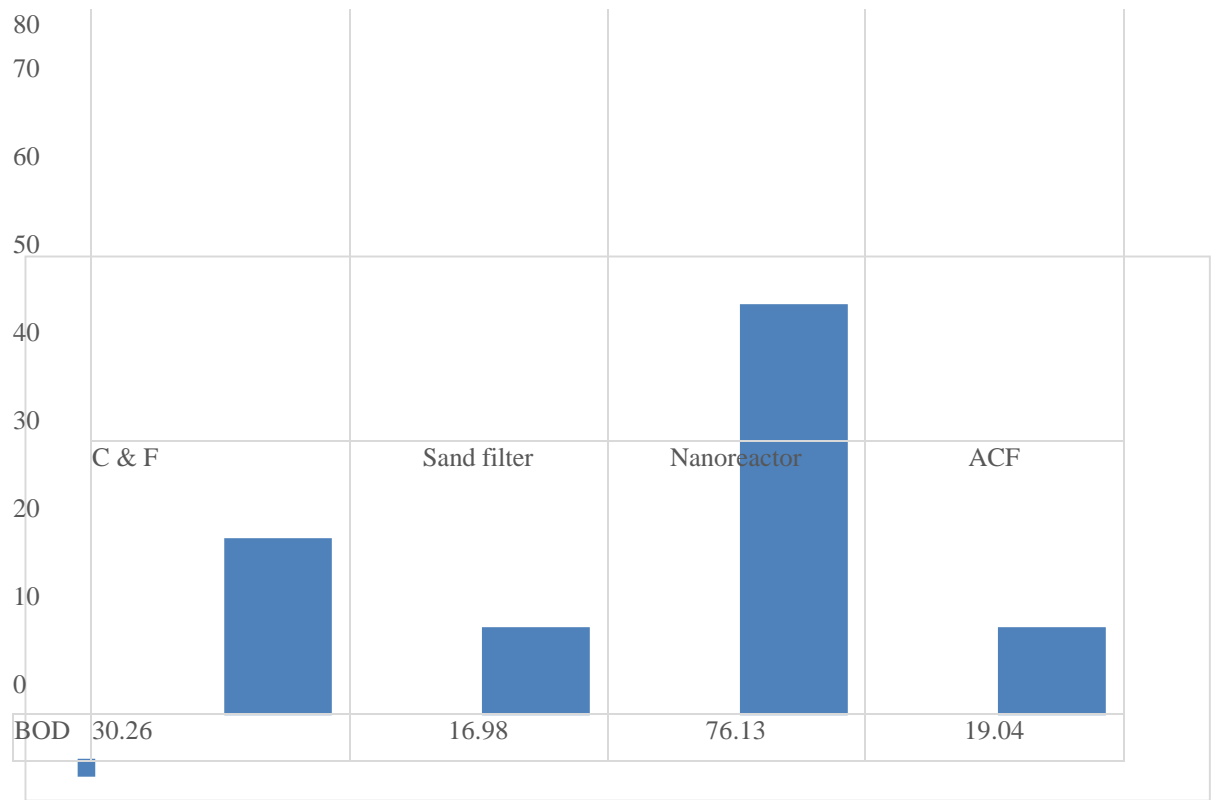


Figure 6: percentage change in BOD for observation set 1

Observation Set 2: -

Table 3: observation data for set 2

Parameter	Raw	After coagulation & flocculation	After sand filter	After nanoreactor (Detention time = 4 hr)	After activated carbon filter
BOD (mg/l)	740	495	380	35	25
pH	9.2	8.8	8.3	8.2	8.4
TSS (mg/l)	1430	310	76	61	12
TDS (mg/l)	3790	3540	3260	2950	2850

Table 4: percentage reduction after individual treatment for set 2, HRT = 4 hr

Parameter	% change from raw to C & F	% change from C & F to sand filter	% change from sand filter to nanoreactor	% change from nanoreactor to ACF	Overall reduction
BOD (mg/l)	33.10	23.23	90.78	28.57	96.62
pH	4.35	5.68	1.20	-2.43	8.69
TSS (mg/l)	78.32	75.48	19.73	80.32	99.16
TDS (mg/l)	6.59	7.90	9.50	3.38	24.80

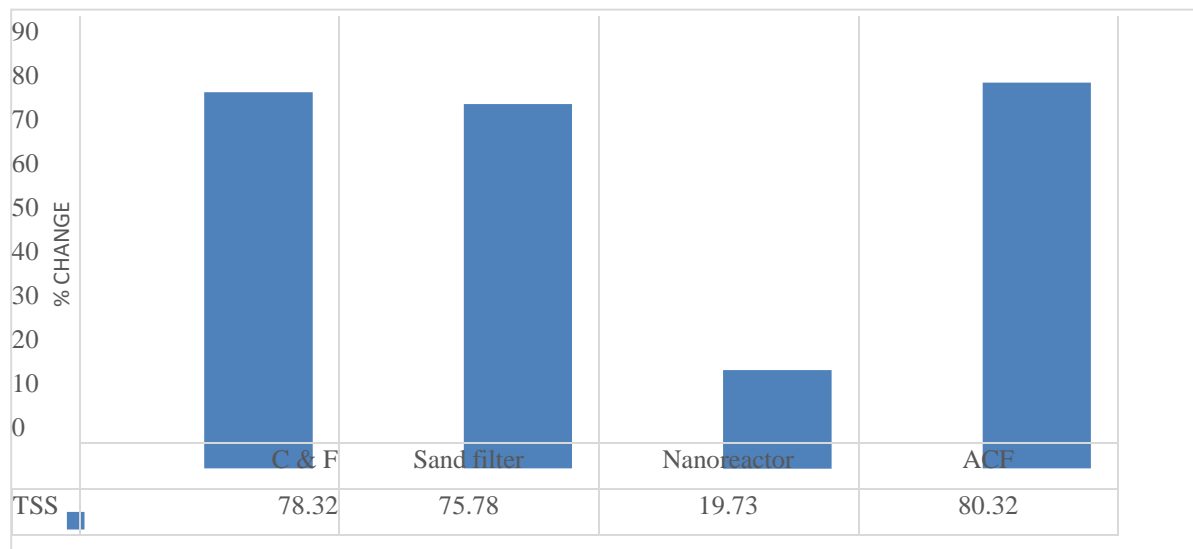


Figure 7: percentage change in TSS for observation set 2

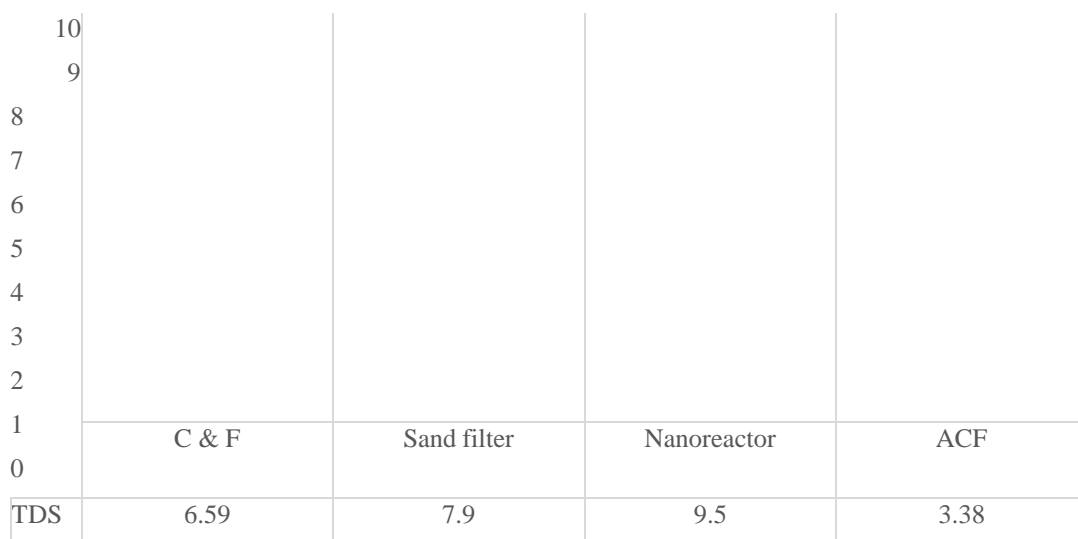


Figure 8: percentage change in TDS for observation set 2

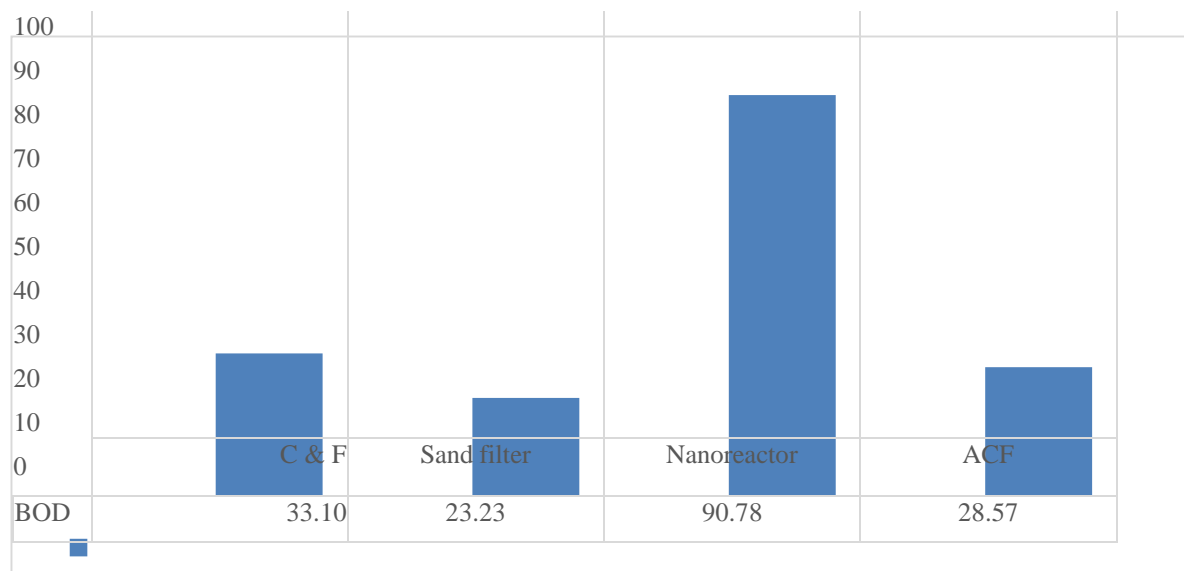


Figure 9: percentage change in BOD for observation set 2

Analysis

The above-presented observations that are for the Galvanized iron plates were summarized and it was found that

For 2 hours' retention time: -

- The pH value ranged from 9.1 at the inlet to 8.6 after the final outlet
- The concentration of BOD reduced from 760 mg/l at the inlet to 85 mg/l after final treatment showing an 88.81 % reduction.
- The TSS concentration reduced from 1363 mg/l to 10 mg/l showing a 99.26 % reduction.
- The TDS concentration reduced from 3710 mg/l to 2880 mg/l showing a 22.37 % reduction.

For 4 hours' retention time: -

- The pH value ranged from 9.2 at the inlet to 8.4 after the final outlet
- The concentration of BOD reduced from 740 mg/l at the inlet to 25 mg/l after final treatment showing a 96.62 % reduction.
- The TSS concentration reduced from 1430 mg/l to 12 mg/l showing a 99.16 % reduction.
- The TDS concentration reduced from 3790 mg/l to 2850 mg/l showing a 24.80 % reduction.

4 CONCLUSIONS

Clean and potable water is the most important resource for the survival of any living creature on this planet. Another important commodity for human survival is the textile products. In the present era, most of the anthropogenic activities even the textile industry produces wastes that can affect the quality of water to some serious extents. Most of the effluents from the textile industry are high in organic material and contains color. To treat this wastewater many conventional methods are already available and to increase the quality of treatment, researchers are working on some new and better methods. One such method is Photocatalysis using a Nano catalyst. In this work, in order to treat the textile effluent, a Photo catalysis based treatment plant was developed. In this plant Zinc Oxide (ZnO) was used as the catalyst. The catalyst was fabricated on galvanized iron plates. Since the positive effects of photocatalysis on textile effluents have already been studied in various forms, hence in this study a rotating reactor was developed. The GI plates were attached to this reactor and wastewater was retained in them for a retention time of 2 hours & 4 hours, different cycles. The quality of treatment was judged by the percentage change in the concentration of COD, pH, TSS, and TDS. There is always some reduction in the concentration of the treatment parameters in Galvanized iron plate, hence rotating the reactor has been proved to be fruitful. The percentage reduction in the concentration of pH, BOD, TDS, and TSS for galvanized iron plates is most ideal for 4-hour retention time and any further increase in the retention time did not lead to any significant change. The nanofilm work only for about 15 days and re-generation of nano film is required.

Declaration of Conflict of Interest : Authors Proclaim that they have no any Conflict of Interest

REFERENCES

- [1] K. Byrappa, A.K. Subramani, S. Ananda, K.M. LokanathaRai, R. Dinesh, M. Yoshimura, Photocatalytic degradation of Rhodamine B dye using hydrothermally synthesized ZnO, *J. Mater. Sci.* 5 (2006) 44–438.
- [2] M.A. Behnajady, N. Modirshahla, R. Hamzavi, Kinetic study on photocatalytic degradation C.I. acid yellow 23 by ZnO photocatalyst, *J. Hazard. Mater.* 133 (2006)
- [3] N. Daneshvar, D. Salari, A.R. Khataee, Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO₂, *J. Photochem. Photobiol. A: Chem.* 162 (2004)
- [4] Dehghani, M. H., & Mahdavi, P. (2015). Removal of acid 4092 dye from aqueous solution by zinc oxide nanoparticles and ultraviolet irradiation. *Desalination and Water Treatment*, 54(12), 3464-3469
- [5] Tarun Gehlot et al (2021) Use Of Regression Model For Water Parameter Prediction Of Godwar Region IJEP 41(8): 948-952 : Vol. 41 Issue. 8 (August 2021)
- [6] Al-Buriahi, A. K., Al-Gheethi, A. A., Kumar, P. S., Mohamed, R. M. S. R., Yusof, H., Alshalif, A. F., & Khalifa, N. A. (2022). Elimination of rhodamine B from textile wastewater using nanoparticle photocatalysts: A review for sustainable approaches. *Chemosphere*, 287, 132162.
- [7] Abdullah, F. H., Bakar, N. A., & Bakar, M. A. (2022). Current advancements on the fabrication, modification, and industrial application of zinc oxide as photocatalyst in the removal of organic and inorganic contaminants in aquatic systems. *Journal of Hazardous Materials*, 424